

A short review on the comparison between Li battery systems and rechargeable magnesium battery technology

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Abstract

An active metal that should be considered as an anode material in high energy density batteries is definitely magnesium. It is relatively cheap, much safer to use and handle than lithium, and its compounds are usually non-toxic.

Similar to lithium, magnesium is covered by surface films in any ‘inert’ atmosphere that contains atmospheric contaminants, and in most of the relevant electrolyte solutions for batteries. In contrast to lithium where the surface films covering the active metal are Li-ion conductors, surface films formed similarly on magnesium cannot conduct the bivalent Mg²⁺ ions. We developed new electrolyte solutions based on ethers of the ‘glyme’ family and magnesium aluminates whose electrochemical window is 2.5 V wide. The efficiency of Mg deposition–dissolution cycles in these solutions is higher than 99%. We also showed that it is possible to construct rechargeable Mg batteries using these electrolyte solutions and cathodes of the Mg_xMoS_y type (chevrel phase), which operate at 1–1.5 V, and can deliver more than 1000 charge–discharge cycles. Some technical details of these battery systems are discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In order to obtain battery systems of high energy density, highly reactive components should be used, i.e. anode materials of the lowest redox potential possible, and cathode materials whose redox potential is sufficiently high compared with that of the anode, thus enabling the composition of battery systems of high working potentials. Natural candidates for anode materials for high energy density batteries are active metals such as lithium, magnesium, calcium, etc. A good introduction to the field of magnesium electrochemistry is obviously a short description of the more established and understood world of lithium batteries. From many points of view, the very complicated behavior of magnesium electrodes can be better understood by comparison with that of lithium electrodes in non-aqueous electrolyte systems. During the last three decades there have been extensive efforts to develop rechargeable batteries with

lithium metal anodes, but these have met with very limited success [1]. Such batteries require the use of non-aqueous electrolyte systems that may either be solid (e.g. Li-ion conducting polymers) or liquid, based on polar aprotic solvents (typical examples of which are organic ethers, esters and alkyl carbonates) [1]. It should be noted that on a thermodynamic basis, lithium metal reacts readily with any relevant polar aprotic solvent, many commonly used salt anions (e.g. ClO₄⁻, AsF₆⁻, PF₆⁻, BF₄⁻, N(SO₂CF₃)₂⁻), and unavoidably present atmospheric contaminants (e.g. H₂O, O₂, CO₂, N₂). Nevertheless, Li metal is apparently stable in many polar aprotic systems due to its coverage by electrically insulating, passivating surface films. These films are formed due to the reduction of solution components by the active metal, which forms insoluble Li salts that precipitate on the lithium surface. It appears that many Li salts such as LiX (X = F, Cl, Br), Li₂CO₃, Li₂O, LiOH, LiOR, LiOCO₂R (R = alkyl group) when precipitated on lithium as thin surface films, are Li-ion conductors. Hence, the lithium metal in the relevant electrolyte solution is electrochemically active in spite of its passivation by the surface films [2].

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This operational situation for Li metal anodes in battery systems limits their reversibility and may lead to severe safety problems in abuse cases such as short circuit, overcharge and exposure to air.

Consequently, the major efforts in this field were shifted towards R&D of Li-ion batteries in which Li metal anodes are replaced by carbonaceous materials that can insert lithium reversibly at potentials close to that of the Li/Li⁺ couple. It should be noted that the electrochemical behavior of Li-C electrodes is also controlled by surface films of similar structure as those formed on lithium electrodes in the same solutions [3]. However, changing the anodic reaction from Li dissolution-deposition to Li intercalation-deintercalation (discharging-charging processes, respectively) leads to a considerable gain in stability, reversibility and enhanced safety (at the expense of some loss in energy density). Li-ion batteries in which the anodes are Li-C insertion compounds, the cathodes are Li_xMO_y insertion materials (M = transition metal oxide such as Mn, Ni, Co, V), and the electrolyte systems are organic polar aprotic solution, have become a commercial reality in recent years and their distribution on the market increases impressively each year. Today the state-of-the-art of these batteries includes features such as gravimetric energy density >150 Wh/kg, wide temperature range of operation ($-30^{\circ}\text{C} < T < 60^{\circ}\text{C}$) and the possibility of obtaining many hundreds of full capacity, charge-discharge cycles [4]. In any event, these battery systems cannot fulfill the increasing needs of the global battery market. Li-ion batteries are relatively expensive and suffer from some safety limitations which put a question mark on the possibility of upscaling them to large batteries that can be used in electric vehicles and/or replace the commonly used lead acid car batteries (which are highly problematic from an environmental point of view because of the lead).

In conclusion, there is an urgent need for R&D of additional new rechargeable battery systems which will be made of cheap and environment friendly materials suitable for upscaling to large sizes, e.g. for electric vehicles, car batteries and load leveling application. A natural candidate as an anode material for high energy density batteries is obviously magnesium. Mg compounds (mostly MgCO₃) are highly abundant in the earth and are environment friendly.

In terms of battery application, the redox potential of the Mg/Mg²⁺ couple is 1 V higher than that of the Li/Li⁺ couple. In addition, the charge capacity of Mg (2233 mAh/g) is lower than that of lithium (3829 mAh/g). However, assuming that it is possible to develop cathode materials of the Mg_xMO_y or Mg_xMS_y type (M = transition metal) for these batteries (analogous to those developed for Li and Li-ion batteries [4]), one can predict that Mg batteries may have an energy density >100 Wh/kg. This is more than twice the energy density of leading rechargeable batteries such as lead acid or Ni-Cd battery systems [5]. The expected lower energy density of Mg batteries in comparison with Li-ion batteries may be compensated for by enhanced safety, cheap

prices and ease in their waste management. Indeed, in the scientific literature of recent years, there are a few reports on R&D efforts on Mg batteries. Several research groups tried to develop primary aqueous and non-aqueous Mg batteries [6]. The development of rechargeable Mg batteries requires the use of polar aprotic electrolyte systems analogous to the above-described Li battery systems. Similarly to lithium, Mg also reacts spontaneously with atmospheric components (O₂, H₂O, CO₂), many polar aprotic solvents and commonly used salt anions (e.g. ClO₄⁻, BF₄⁻, SO₃CF₃, etc.) [7]. Hence, in most of the relevant liquid electrolyte solutions, this active metal is covered with passivating surface films which are insoluble organic and inorganic Mg salts formed by the thermodynamically favorable reactions of Mg with the above solutions components [7].

However, in contrast to the surface films formed on lithium in non-aqueous, polar aprotic electrolyte solutions, which are usually Li-ion conducting, the surface films formed on magnesium in the same solutions cannot conduct the bivalent Mg ions. Thereby, electrochemical Mg dissolution in most of the commonly used polar aprotic solutions occurs at relatively high overpotential, via a mechanism which involves a breakdown of the surface films, and electrochemical deposition of magnesium on Mg electrodes covered by passivating surface films is impossible [7]. It is well known that Mg can be electrochemically reversibly deposited and dissolved in ethereal/Grignard salt solutions (RMgX, R = alkyl, aryl groups and X = Cl, Br) [8]. We recently studied these systems and concluded that these processes are possible because the magnesium surfaces in these solutions do not develop stable passivating surface films. However, Mg deposition processes in these solutions are far from being simple, two-electron redox processes, but rather are complicated and involve adsorption phenomena [9].

In any event, despite the very high reversibility of Mg electrodes in these solutions, they are not at all suitable as electrolyte solutions for battery application due to their very poor anodic stability. Their electrochemical window is too narrow to make an ethereal/RMgX solution compatible with any possible relevant cathode material for Mg batteries [7]. About 9 years ago, Gregory et al. suggested the use of ethereal solutions of Mg(BR₄)₂ solutions (R = various alkyl or aryl groups) as good candidates for rechargeable Mg batteries [10]. They showed that these electrolyte solutions have a wider electrochemical window compared with the Grignard salt solutions, and that they can be compatible with Mg insertion compounds such as Mg_xCoO_y. These authors also reported on attempts to compose rechargeable Mg battery systems based on the above solutions and a Mg_xCoO_y cathode [10]. However, the results presented in the literature are far from being convincing that the above systems are indeed practical in terms of stability and reversibility. In recent years we have also seen continuous efforts towards the exploration and development of transition metal oxides that can insert bivalent metal cations in non-aqueous media,

including Mg ions [11]. However, since the publication of Gregory et al. appeared, we have not to date seen any report on R&D of integral, practically important, non-aqueous rechargeable magnesium battery systems.

Over the past years we have thoroughly studied the electrochemistry of Mg electrodes in non-aqueous systems [7,9] as well as the electrochemistry of a variety of intercalation electrodes in different solutions [12]. Based on these studies, we developed a rechargeable magnesium battery system which may have considerable commercial importance, as recently reported [13]. The R&D efforts involved the use of the most sophisticated and novel tools in modern electrochemistry with the emphasis on the use of in situ methods. These included in situ FTIR spectroscopy, and electrochemical quartz crystal microbalance (EQCM) in conjunction with impedance spectroscopy (EIS) in simultaneous experiments, and scanning probe microscopy (atomic force and scanning tunneling microscopies, AFM and STM) [9,13]. We present herein some typical features related to the components of these battery systems. The basic experimental details related to this R&D effort (synthetic routes, instrumentation, analytical techniques, etc.) were already described [7,9,12,13].

2. Results and discussion

Fig. 1 shows steady-state cyclic voltammograms of electrodes of four different ethereal solutions (as indicated) of one of the Mg-Al complexes that we developed: $Mg(AlCl_2EtBu)_2$. They reflect reversible Mg deposition, dissolution and electrochemical windows wider than 2 V. The possibility of using ethers of different properties (boiling point, viscosity, melting point, etc.) is important for achieving very good low and high temperature performance with the rechargeable Mg batteries. Fig. 2 shows a typical galvanostatic cycling efficiency test for a Mg anode in a $Mg(AlCl_2EtBu)_2/THF$ solution. Magnesium (with a charge X in C) was deposited on copper, followed by repeated charge-discharge cycling of about 20% of the active metal initially deposited, at 0.5 mA/cm². After 80 cycles, the residual Mg was dissolved. These experiments reflect cycling efficiency close to 100% and low interfacial resistance during dynamic Mg deposition-dissolution (the overvoltage around 0.1 V is mostly due to the solution resistance).

The cathode that we developed ($MgMo_3S_4$, chevrel phase) is described in [13]. Fig. 3 shows typical steady-state cyclic voltammograms of the $Mg_xMo_3S_4$ cathodes (composite

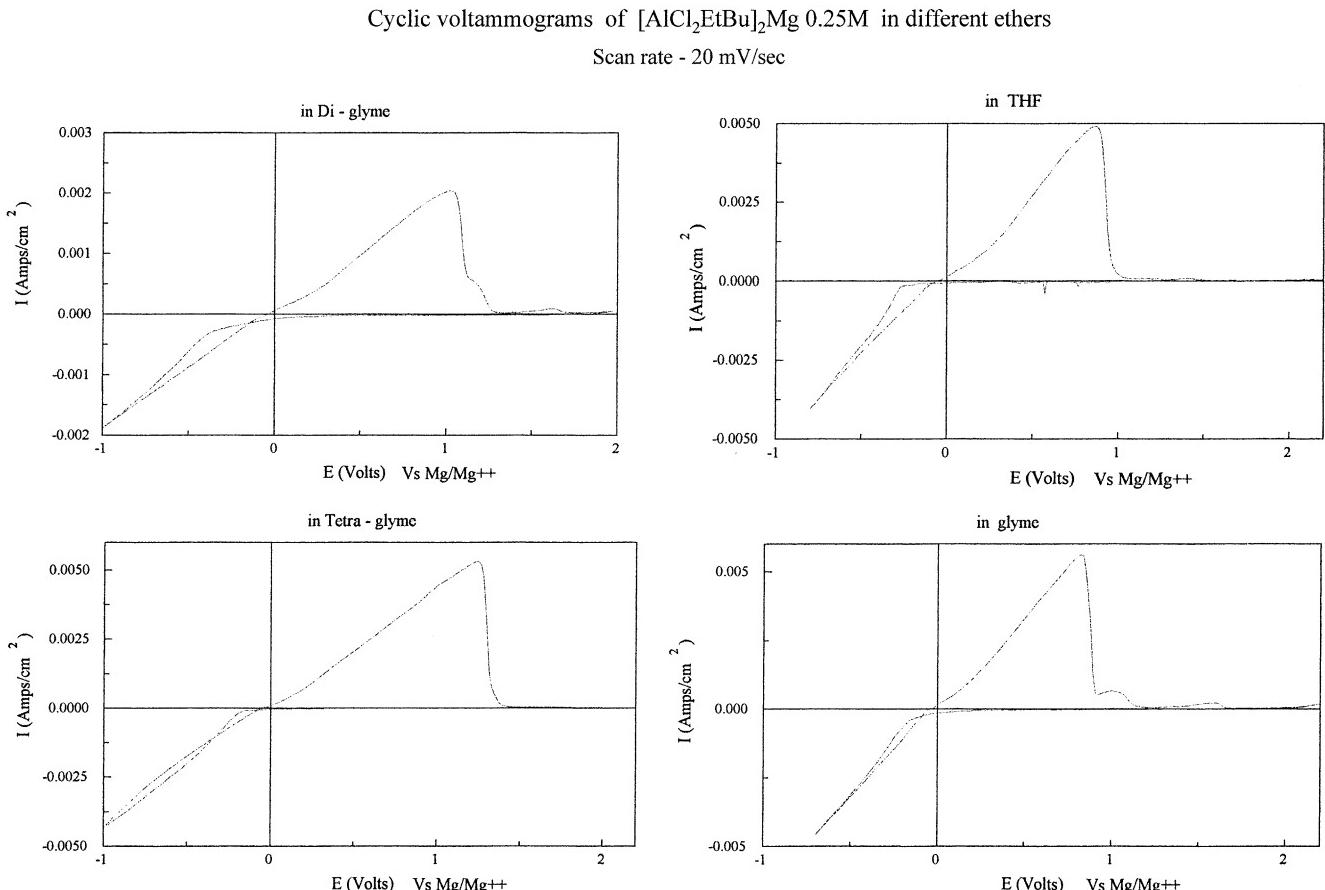


Fig. 1. Steady-state cyclic voltammograms of $Mg(AlCl_2EtBu)_2$ solutions in four different ethers, as indicated. Pt working electrodes are used. The potential scan rates are indicated.

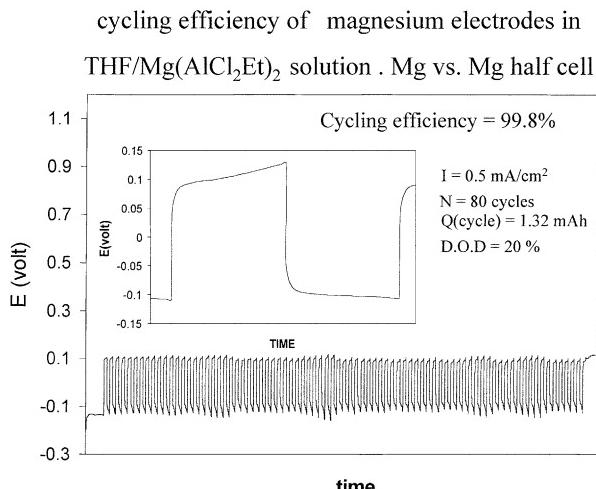


Fig. 2. A typical galvanostatic cycling efficiency test of a Mg anode in a $\text{Mg}(\text{AlCl}_2\text{BuEt})_2/\text{THF}$ solution: Cu substrate, 0.5 mA/cm^2 .

electrodes containing PVDF and carbon black 10% each, see technical details in [13]) in three different solutions, as indicated in the figure. The behavior in the $\text{Mg}(\text{BPh}_2\text{Bu}_2)_2/\text{THF}$ solution, which is the electrolyte solution suggested for rechargeable Mg batteries by Gregory et al. [10] reflects very slow kinetics. The kinetic differences in the cathode behavior in the two THF solutions, as presented in Fig. 3, reflect different structures of Mg complexes in the Mg-aluminate and the Mg-borate solutions from which Mg ions have to be released and inserted into the lattice of the Mo_3S_4 material. It can be seen that the kinetics of the cathode in the $\text{Mg}(\text{ClO}_4)_2/\text{ACN}$ solution are the fastest, because in this solution the Mg insertion process does not involve structural changes of complicated Mg complexes, as in the ethereal solutions. The electrochemical measurements of these cathodes show that about 0.6–0.85 atoms of magnesium can be inserted reversibly per each Mo_3S_4 unit (corresponding to a maximal practical capacity of 100 mAh/g).

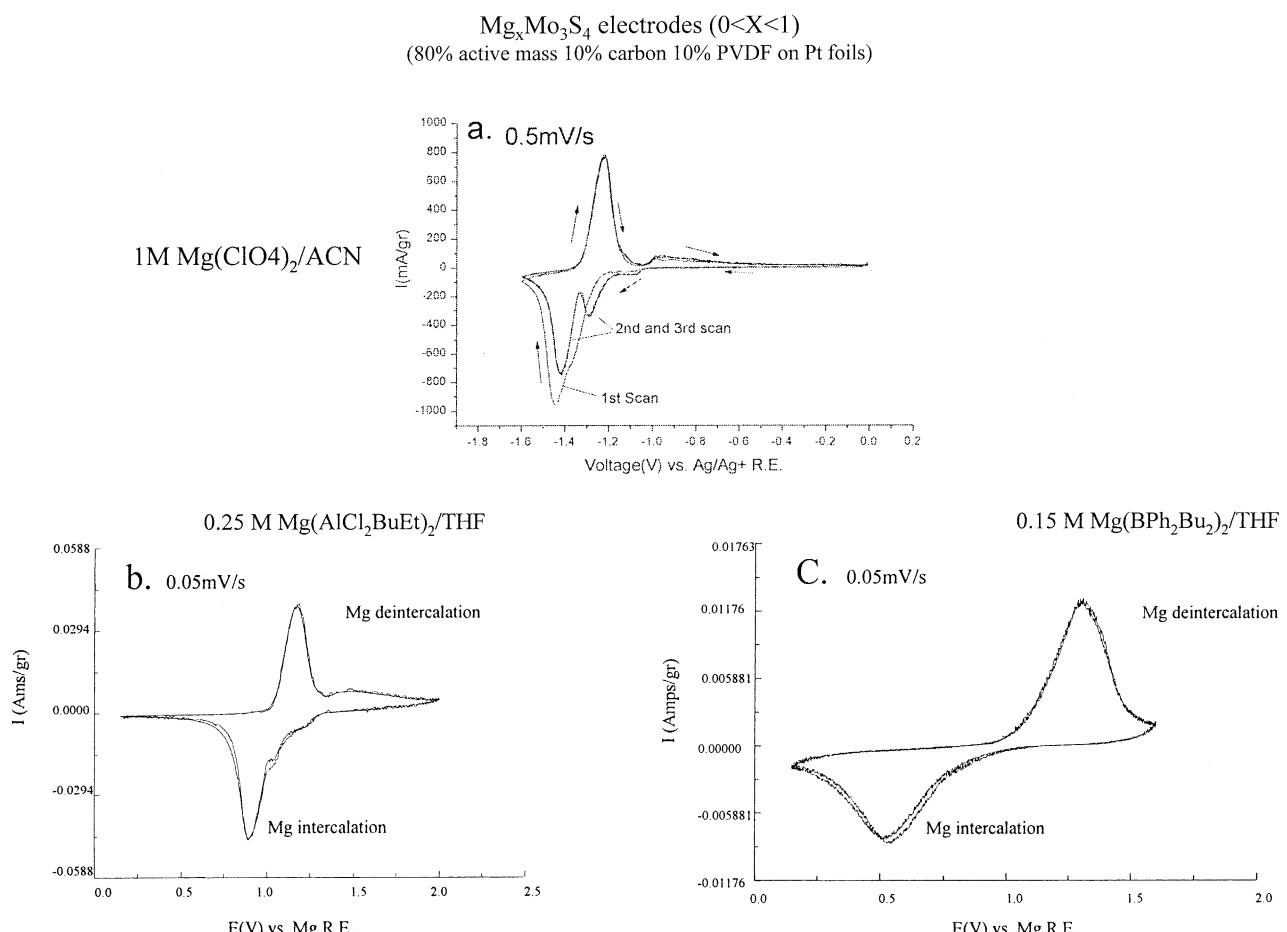


Fig. 3. Typical steady-state cyclic voltammograms of Mo_3S_4 composite electrodes (80% active mass, 10% carbon black, 10% PVDF binder and Al current collector) in 1 M $\text{Mg}(\text{ClO}_4)_2$ /acetonitrile, 0.25 M $\text{Mg}(\text{AlCl}_2\text{BuEt})_2/\text{THF}$ and 0.15 M $\text{Mg}(\text{BPh}_2\text{Bu}_2)_2/\text{THF}$ solutions. The potential scan rates are indicated. In the ACN solution, Hg/Mg amalgam and Ag wire served as counter and pseudo reference electrodes, respectively. In the THF solutions, Mg foil and wire served as counter and reference electrodes.

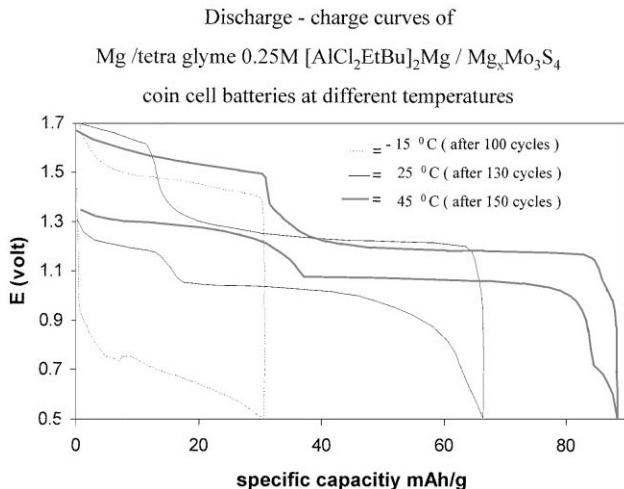


Fig. 4. A few representative discharge-charge curves of rechargeable Mg/tetraglyme — 0.25 M $Mg(AlCl_2EtBu)_2/Mg_xMo_3S_4$ batteries in coin cell configuration at different temperatures as indicated. The current densities ranged between 0.1 and 0.15 mA/cm². The relevant cycle number for each curve is indicated.

Fig. 4 shows typical charging curves of rechargeable coin cell Mg batteries at different temperatures. The cycle number and capacity (calculated based on the weight of the two working electrodes) are indicated. These battery systems can be cycled more than 1000 times with capacity fading <10–15%. The possible temperature range of operation seems to be at least between –30 and 60°C.

3. Conclusion

The prototypes of rechargeable Mg batteries that we presented herein have a working voltage around 1.0–1.2 V, and can reach an energy density around 80 Wh/kg of the battery core (electrodes and solution layer). The cycling

behavior of these battery systems is excellent, i.e. >1000 full DOD charge-discharge cycles at a wide temperature range. These batteries cannot compete with any type of Li or Li-ion battery in terms of energy density and high operational voltage. However, these new battery systems may be a cheap, ‘green’ and safe substitute for heavy load, dangerous and environmentally problematic Ni–Cd and lead acid battery systems.

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